

The Phase Diagram of the High-Density Polyethylene–*m*-Xylene System

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Received December 19, 2014;

Revised Manuscript Received January 12, 2015

Abstract—A phase diagram of the high-density polyethylene (HDPE)–*m*-xylene system has been plotted and discussed in the context of the concept according to which semicrystalline polymers are three-dimensionally structured liquids with thermotropic grid nodes in the form of crystallites from the thermodynamic point of view. It has been shown that the specific feature of the semicrystalline-polymer–good-solvent systems is the change in the number of phases in them that is exclusively due to the reversible process of dissolution of the low-molecular-mass component in the amorphous regions of the polymer. It has been proposed that the coordinates of the imaging point that corresponds to the minimum temperature of the complete amorphization of the polymer in the presence of the liquid in the phase diagram of these systems can be used as a characteristic for the level of the thermodynamic affinity of the semicrystalline polymer and the liquid.

DOI: 10.1134/S0965545X15030086

INTRODUCTION

According to [1], semicrystalline polymers, in terms of the phase state, are specific liquids with three key features.

(i) They are distinctly and consistently heterogeneous at the microlevel but homogeneous like the Gibbs phases [2] because the structural parameters of macrosamples of all sizes are the same.

(ii) They are thermodynamically nonequilibrium because of the incompleteness of the process of crystallization of the elementary units of the macromolecules and are internally strained (metastable [3]) because of the physical inseparability of the microvolumes with a different level of order in the spatial disposition of the elementary units.

(iii) From the structural–chemical point of view, these are crosslinked polymers with thermotropic grid nodes in the form of crystallites, in which (as opposed to vulcanized elastomers) the volumes of the nodes and intermodal regions are comparable.

Hence, if a parallel is drawn between the processes occurring in the semicrystalline-polymer–liquid systems and in the binary mixtures of low-molecular-mass substances, the process of mixing of two liquids, one of which is a high-molecular-mass liquid in a physical state that is not equivalent to the liquid state of matter, should be considered.

The phase diagram of such a liquid from the thermodynamic point of view of a binary system should, apparently, include two limiting lines: namely, a phase line reflecting the temperature–concentration limit of the change in the number of phases in the system and

a nonphase line characterizing the change in the physical state of the high-molecular-mass liquid as a result of the dissolution of the low-molecular-mass liquid in it.

Indeed, this fact should be taken into account during selection of an experimental method for the study of such binary systems.

In this study, the phase diagram of the high-density polyethylene (HDPE)–*m*-xylene system plotted by us in the context of the outlined concept is discussed in detail.

EXPERIMENTAL

HDPE of the 293–285 D brand (OAO Kazan'orgsintez) with a melting point of 411.0 ± 1.0 K (determined with a portable heated stage of the Boetius type equipped with a PHMK 05 optical microscope at a rate of heating of 4 K/min (VEB Analytik)), a melt-flow index of 0.054 ± 0.0005 g/10 min (DIN EN ISO 1133:2009), and a density of 0.934 ± 0.008 g/cm³ at 298 K (picnometrically determined) and high-purity grade *m*-xylene with a refractive index corresponding to the reference data [4] were used in this study. Before the experiment was started, HDPE was kept under stirring for 5 h in a sevenfold excess by mass of *m*-xylene at 368 K to remove fractions that do not participate in the formation of the crystallites.

During plotting of the phase diagram of the considered system, a method that was earlier described in detail [5] was used. This method includes the observation of the state of the polymer–liquid binary system

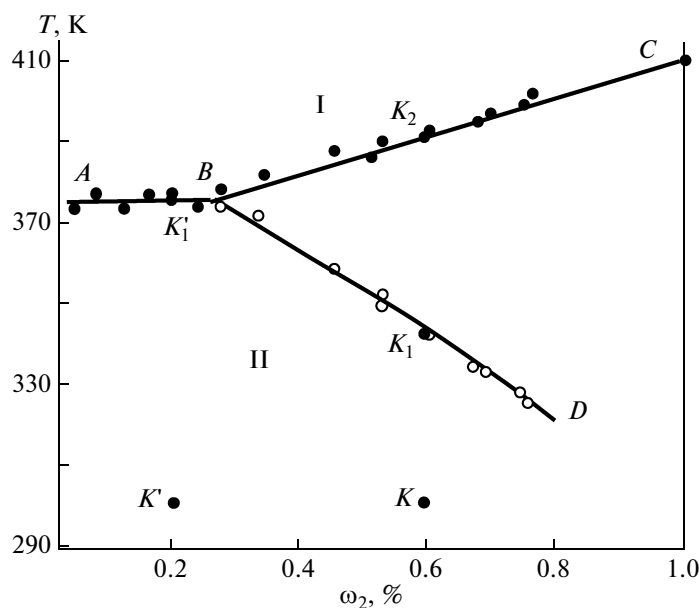


Fig. 1. Phase diagram of the HDPE-*m*-xylene system. For explanation, see the text.

placed into a glass ampoule with an internal diameter of 3 mm and volume of 0.3 cm³ and examined under a horizontal microscope during stepwise heating.

This method makes it possible to record the temperatures of the following four events occurring during the heating of the initial two-phase system: (i) the liquid present in the initial mixture dissolves in the polymer completely, but the latter remains semi-crystalline (continues to opalesce); (ii) the polymer is completely amorphized as a result of the additional heating of this single-phase system (the opalescence disappears); (iii) the polymer is completely amorphized (no opalescence is present), while the liquid present in the initial mixture has not completely dissolved in it yet (two liquid phases coexist); and (iv) the two-phase liquid system turns into a single-phase system.

RESULTS AND DISCUSSION

Line *BD* was plotted with respect to the values of the temperature that correspond to the first of the specified events; line *BC*, with respect to the values of the temperature that correspond to the second of the specified events; and line *AB*, with respect to the values of the temperature that correspond to the third and fourth of the specified events (Fig. 1).

Let us illustrate the character of the change in the state of the considered system during an increase in temperature with the use of the photographs presented in Fig. 2.

The system containing 0.6 weight parts of HDPE is two-phase at point *K*; thus, the polymer bead and the liquid coexist (Fig. 2a).

An increase in the size of the polymer bead, accompanied by a simultaneous decrease in the amount of *m*-xylene, is observed during stepwise heating (holding at each temperature for some time [5]) of the system. The single-phase microheterogeneous system occurs at point *K*₁: Namely, *m*-xylene dissolves completely in the amorphous regions of the polymer, but the polymer remains opalescent (Fig. 2b). This opalescence disappears completely at point *K*₂, a result that is evidence of the completion of the process of amorphization of the polymer and the formation of a molecular mixture of HDPE and *m*-xylene (Fig. 2c).

The state of the system containing 0.2 weight parts HDPE at point *K*' is similar to that at point *K*.

Two processes were recorded at point *K*₁. First, the polymer bead turned into an optically transparent liquid (the lower layer in Fig. 2d), and then (after ~6 h) the boundary between the two optically transparent liquids disappeared (Fig. 2e).

A similar behavior was observed at 375 K for all the mixtures containing *m*-xylene in amounts greater than (1 - ω_{2,B}) weight parts.

Line *ABD* is the phase line in the discussed diagram. The system is two-phase below the specified line: a clear liquid and a saturated solution of this liquid in the amorphous regions of the polymer.¹

This circumstance means that the osmotic equilibrium is reached in the system in this temperature—

¹ How the position of line *BD* on the temperature-concentration field is independent of whether it is obtained via the optic method used in this study or via the direct determination of the temperature dependence of the solubility of the liquid in the amorphous regions of the semicrystalline polymer was shown in [6].

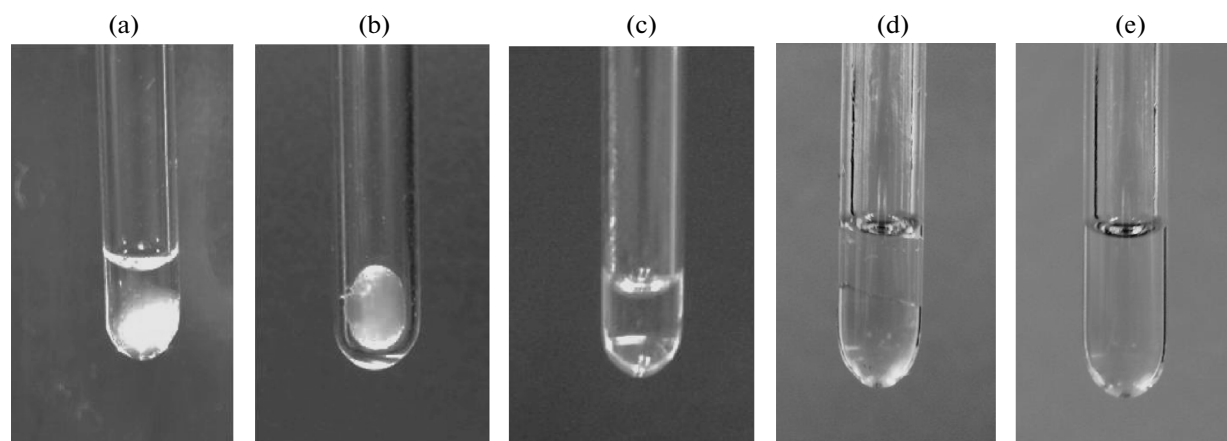


Fig. 2. Photographs of the HDPE–*m*-xylene system at temperatures corresponding to the points (a) K , (b) K_1 , (c) K_2 , and (d, e) K_1 .

concentration region, while the three-dimensionally structured high-molecular-mass liquid is itself an osmotic cell.

When the composition of the initial mixture corresponds to point B and T_{am}^{min} (the minimum temperature of the complete amorphization of the semicrystalline polymer in the presence of the liquid), the nodes disintegrate completely and the heterogeneous mixture turns into a solution of the liquid in the amorphous polymer.

The temperature of such a transition in the considered system (375 K) turns out to be so high that the formed molecular mixture of HDPE and *m*-xylene hereinafter mixes indefinitely with any excess of the latter.

In practice, this situation will manifest itself in such a way that the mixture of HDPE and *m*-xylene containing 0.73 or more weight parts of the low-molecular-mass component will turn into a homogeneous molecular mixture at $T \geq 375$ K.

From the thermodynamic point of view, the possibility of the occurrence of such a situation is the consequence of the fact that, in the semicrystalline-polymer–good-solvent systems, the change in the number of phases is associated exclusively with the processes of dissolution of the liquid in the amorphous regions of the polymer during the heating of the system and segregation from them during cooling of the system.

Thermodynamic characteristics of certain semicrystalline-polymer–liquid systems

System	T_m , K	T_{am}^{min} , K	$1 - \omega_{2,B}$	β
LDPE–toluene	384.6	341.0	0.90	0.61
PP– <i>m</i> -xylene	449.9	397.0	0.78	0.70
HDPE– <i>m</i> -xylene	411.0	375.0	0.73	0.74

In addition, the presence of thermotropic nodes of the three-dimensional grid in specific liquids such as semicrystalline polymers makes itself evident by the fact that single-phase region I is divided into two parts (subregions) by limiting line BC .

Above line BC , there is a subregion of the homogeneous molecular mixtures of high-molecular-mass and low-molecular-mass components, while below line BC , there is a subregion of single-phase thermoreversible gels whose physical state changes from viscous flow to solid as it draws near line BD .

However, the transition across this line to area II may be accompanied by the formation of both equilibrium single-phase and metastable two-phase gels (depending on the rate of cooling), which are of interest as precursors during the molding of polymer membranes with adjustable levels of porosity.

CONCLUSIONS

Note that the coordinates of imaging point B are an important thermodynamic characteristic of the semicrystalline-polymer–liquid system.

Apparently, the trend $\omega_{2,B} \rightarrow 0$, $T_{am}^{min} \rightarrow T_m(L)$, where $T_m(L)$ is the melting point of the low-molecular-mass component, should occur with an increase in the thermodynamic affinity of the high-molecular-mass and low-molecular-mass components.

Hence, it is reasonable to use a combination of two variables as a criterion for the quantitative estimation of the thermodynamic affinity of the components of any semi-crystalline polymer–liquid system: namely, (i) the relationship $T_{am}^{min}/T_m = \beta$, which characterizes the degree of the decrease in the melting point of the last crystallites of the polymer due to the dissolution of the liquid in it, and (ii) $1 - \omega_{2,B}$, the weight part of the

liquid, whose presence in the initial mixture makes it possible to reach T_{am}^{\min} .

The table compares the values of these parameters for the semicrystalline-polymer-liquid systems discussed in this paper and two semicrystalline-polymer-liquid systems earlier studied by us [5, 6]. The thermodynamic affinity in the polyolefin-alkylbenzene systems changes in the following sequence: LDPE-toluene > PP-*m*-xylene > HDPE-*m*-xylene.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 12-03-97514).

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Translated by E. Boltukhina